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Thermal analysis technique for investigating gelation of rigid PVC compounds

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INTRODUCTION

In order to produce rigid products, PVC powder is frequently blended with the necessary additives (including stabilizers, lubricants and processing aids) in a high speed mixer and then processed by an appropriate method, most commonly extrusion. During processing the powder grains (approximately 100 μm in diameter) are broken down to produce a continuous network. These changes are usually referred to as gelation or fusion, and, since the level of fusion is an important factor in determining the mechanical strength and fracture behaviour of processed products, various techniques for determining gelation have been investigated. Early methods used for this purpose include measurement of mechanical properties (requiring a relatively large amount of sample in a specified physical form), and solvent immersion tests, in which a processed sample is placed in a solvent such as acetone or dichloromethane. In the latter tests the sample swells and particle boundaries become detectable in partly fused samples, but later stages of fusion are not differentiated. More recently a number of workers[1-5] have used a rheological method to assess the level of fusion. Samples are extruded using a capillary viscometer with a short or effectively zero length die (*L*/*D* ratio 1 to 3). The pressure on the piston is due to elastic deformation of material at the capillary entry, and is correlated with level of fusion which produces an increasingly elastic melt. Extrusion pressures for 'unknown' samples are compared with a standard curve produced from samples of the same compound processed to various known temperatures.

In this work, the use of thermal analysis for assessing gelation or fusion levels is proposed. Results obtained are compared with results from the rheological method.

EXPERIMENTAL

Two PVC compounds were examined. Both compounds were dry blended using a Fielder 8-litre high speed mixer.

In *Table 1* compound 1 was processed to a range of temperatures using a Brabender Plastograph, while compound 2 was compression moulded at a range of temperatures. Cooling was carried out under controlled conditions; it would not of course be identical for the two types of sample.

For the thermal analysis experiments, 10 mg samples were heated from room temperature to 240°C at 20°C per min using a Du Pont 990 Thermal Analyser fitted with a d.s.c. cell. Results are shown in *Figure 1* for compound 2. For the rheological test, samples were extruded using a Davenport Extrusion rheometer fitted with a die of length

Table 1

	Parts by weight	
	Compound 1	Compound 2
Breon S110/11 (suspension PVC)	100.0	–
Corvic D55/09 (suspension PVC)	–	100.0
Dibasic lead stearate	2.5	–
T-135 Thiotin stabilizer	–	3.0
Calcium stearate	0.4	0.5
GS Wax 2411P	0.3	–

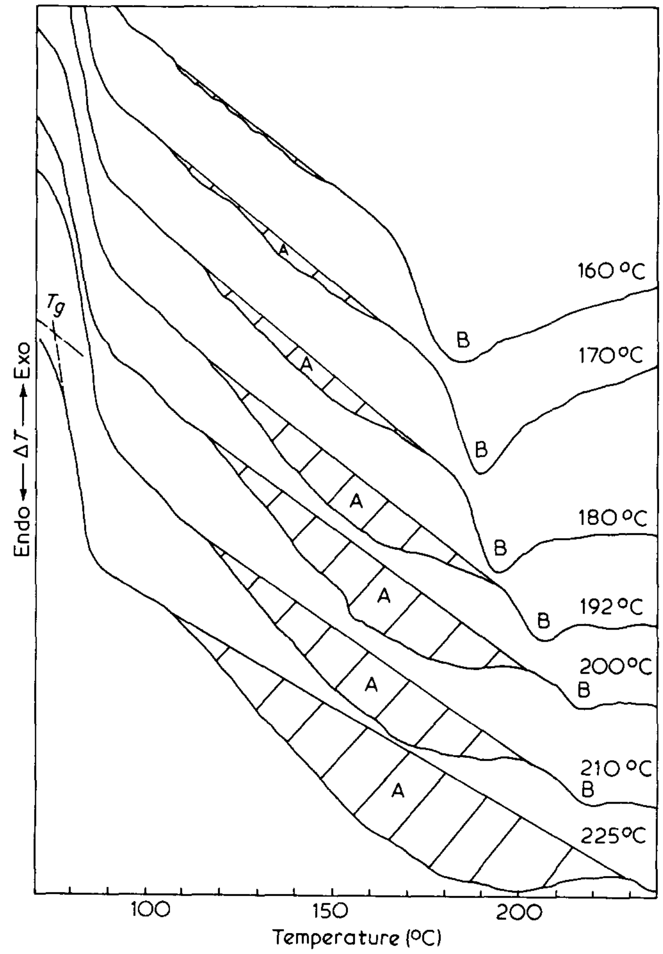

Figure 1 D.s.c. thermograms of compound 2 compression moulded at various temperatures

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[*] At present: B. F. Goodrich Chemicals Ltd., Technical Centre, Avan Lake, Ohio, USA.

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0.85 mm and diameter 2.25 mm. Measured extrusion pressures are plotted in *Figure 2* for the two series of samples.

DISCUSSION

In *Figure 1*, three features are observed in the d.s.c. traces. First, an endothermic baseline shift corresponds to the glass transition temperature of the polymer. In addition there are two endothermic peaks. The broad peak B represents the melting of crystallites of various sizes and degrees of perfection and is obtained for an unprocessed polymer blend. It is seen that this peak decreases in size and shifts to a higher temperature as the processing temperature increases. The size decrease is attributed to melting of less perfect or smaller crystallites, while the temperature shift is caused by annealing of unmelted crystallites. As processing temperature increases endotherm A appears and increases in size. Similar results were obtained for compound 1 processed in the Brabender plastograph at various temperatures. In *Figure 3* the energy of endotherm A is plotted as a function of processing temperature for the two compounds. It is noted that in both cases the steep increase in endotherm enthalpy is found to occur at a similar temperature to the initial increase in extrusion pressure shown in *Figure 2.* Furthermore, a plateau region is observed for the Brabender processed samples by both methods, and the Brabender processed samples produce both higher extrusion pressures and higher peak enthalpies. (This may be due to compound differences or the presence of shear heating in the Brabender). Earlier work in this laboratory[6] haas also shown that endotherm A increases over the same temperature range as yield stress, when tensile properties are measured for a series of compression moulded samples.

It therefore appears that thermal analysis is a potential method for fusion or gelation measurement, although the two methods do not produce identical results, as the final plateau observed by extrusion rheometry for compression mouldings from compound 2 does not occur when peak areas are measured. However, some doubts about the

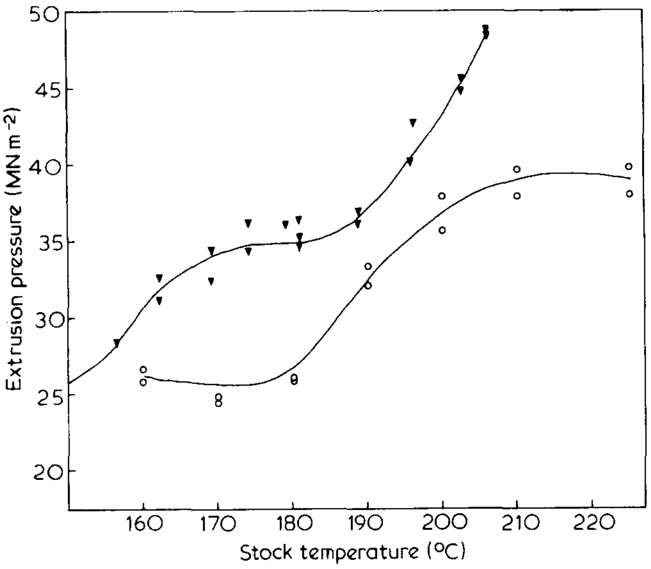

Figure 2 Capillary rheometer extrusion pressure *versus* stock temperature (°C); (▼) Compound 1 processed in Brabender plastograph; (O) Compound 2 compression moulded

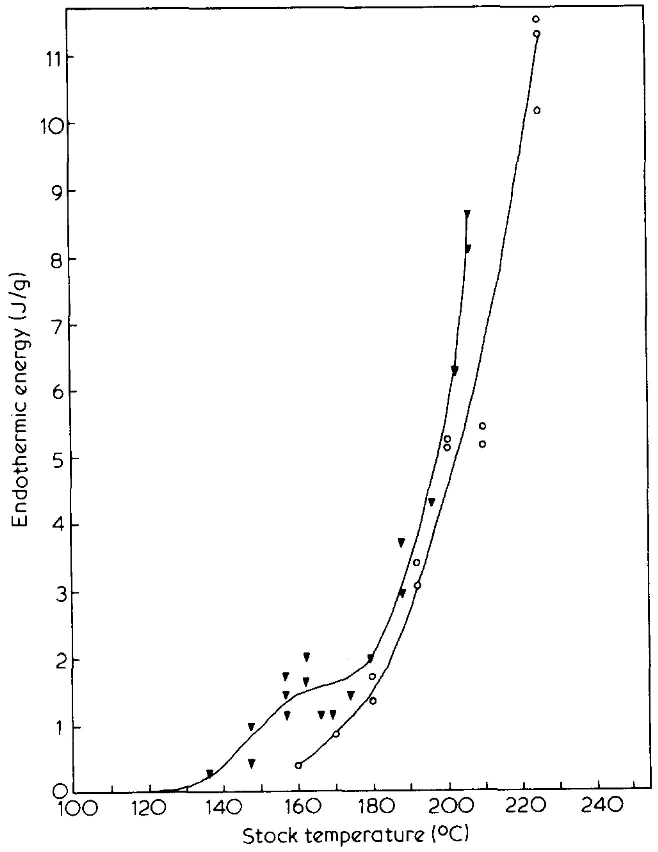

Figure 3 Enthalpy corresponding to peak A *versus* stock temperature (°C); symbols as *Figure 2*

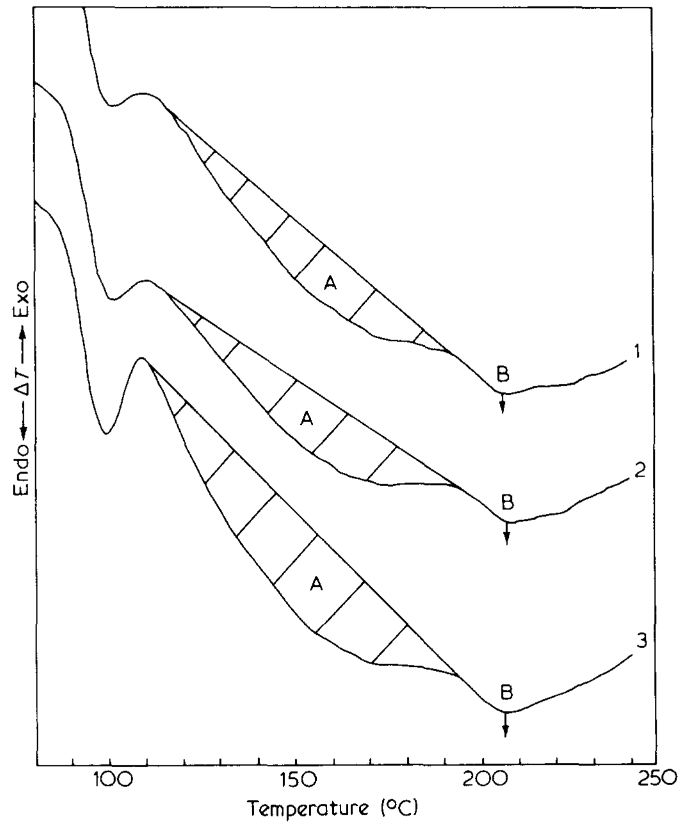

Figure 4 D.s.c. thermograms of extruded samples of compound 1

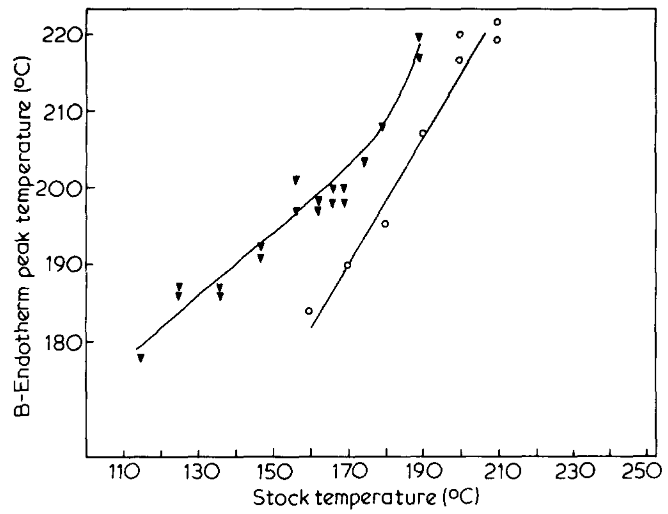

Figure 5 Temperature of peak B (°C) *versus* stock temperature (°C); symbols as *Figure 2*

universal applicability of the rheological method have already been expressed[2], since the standard curve depends on shear history, time and temperature. In order for the technique to be a useful one it must obviously be applicable to processed samples. *Figure 4* shows d.s.c. traces obtained for Compound 1 samples blended under different conditions and extruded using a Leistritz LS-30-34 twin screw extruder. It is noted that endotherms A and B are again discernible. (The peak near 100°C is one which develops on room temperature storage of rigid PVC, due to a slow reduction in free volume[7]). All samples were extruded using the same conditions and it is apparent that peak B is at a similar temperature in all cases, and about 20°C above the temperature at the die (183°C).

It appears therefore that the position of peak B provides information about the maximum temperature to which the polymer has been subjected. *Figure 5* shows how this temperature increases with processing temperature for the two compounds studied. The area of endotherm A appears to be related to the level of fusion. The nature of the endotherm is not yet fully understood, but it is possible that it is due to the formation of imperfect ordered regions which are produced as a continuous PVC network develops, and which subsequently melt on reheating. Further work is being carried out to investigate the changes occuring in the compounds, and the value of this thermal analysis technique in assessing fusion levels.

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A procedure for rapid conditioning of hygroscopic test pieces by humidity cycling

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INTRODUCTION

Tests on hygroscopic polymers often have to be made at moisture contents that are in equilibrium with the air humidities that they will meet in service, such as, for example 60% r.h. Since the polymer has been moulded at a high temperature and therefore starts life very dry, it must be stored in the test humidity for enough time to allow it to reach the new equilibrium moisture content. If the moulding is small this conditioning time may be short but for large mouldings it may be very long. In fact dimensional analysis of the diffusion equation shows that the conditioning time is proportional to the square of the minimum characteristic dimension of a simple-shaped moulding. So, for example, a 1 mm thick nylon-66 sheet will take about 1580 h to reach 98% of equilibrium at 60% r.h. from 0% r.h. at 23°C, whilst a 3.17 mm (1/8 inch) sheet will take about 15 900 h (95 weeks).

EXPERIMENTAL

Various methods have been used to accelerate the conditioning of specimens with elevated temperatures. One method, which has been incorporated in an ISO standard[1] in spite of disapproval on technical grounds by certain Member Bodies including that of the U.K., requires the storage of the samples in an aqueous solution of potassium acetate at a temperature between 95° and 100°C for periods up to 7 days. The Standard claims that no degradation has been experienced within this time limit provided that no additives can migrate into the solution and provided that the specimen's electrical properties are not being measured (since they might be affected by residual salt). The Standard also points out that the mechanical properties may be different from those obtained by normal room-temperature conditioning. Another method[2], aimed at 50% r.h., requires storage

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